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(21) International Application Number: PCT/GB99/03352 (22) International Filing Date: 8 October 1999 (08.10.99) (30) Priority Data: 9822263.1 14 October 1998 (14.10.98) GB 9827177.8 11 December 1998 (11.12.98) GB (71) Applicant (for all designated States except US): ALBRIGHT & WILSON UK LIMITED [GB/GB]; 210-222 Hagley Road, Warley, West Midlands B68 0NN (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ODELL, Barbara [GB/GB]; 3 Courtfield Drive, Charlton Kings, Cheltenham, Gloucestershire GL52 6XW (GB). JONES, Christopher, Raymond [GB/GB]; 110 Sutherland Road, Cheslyn Hay, Nr. Walsall, West Midlands WS6 7BS (GB). TALBOT, Robert, Eric [GB/GB]; 3 Meriden Close, Cannock, Staffordshire WS11 1QG (GB). (74) Agent: BARKER BRETTELL; 138 Hagley Road, Edgbaston, Birmingham B16 9PW (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: LEACHING DIVALENT METAL SALTS (57) Abstract <p>A composition for leaching deposits of divalent metal salts such as ferrous sulphide comprises: A) a tetrakis (hydroxymethyl)phosphonium salt; B) an ammonium salt in a ratio of A:B of from 0.01 to 100:1; and C) sufficient of an acid, which is substantially unreactive with tetrakis(hydroxymethyl)phosphonium ion or ammonium ion to maintain the pH below 4.5. The compositions may be solutions or particulate solids.</p>		

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LEACHING DIVALENT METAL SALTS

The present invention relates to a system for inhibiting the formation of water insoluble divalent metal salt deposits removing or reducing such deposits or of leaching metal therefrom. The said system includes a composition adapted to inhibit or reduce such deposits, a method of making said composition and the use of said composition for the aforesaid purpose.

A number of water insoluble divalent metal salts are associated with problems of scaling or blockage, e.g. in the water treatment and oil industries. Examples include the carbonates and sulphates of calcium and barium. A particular problem in the oil industry is ferrous sulphide which forms extensive deposits in oil wells, obstructing the flow through wells and adjacent strata. Other insoluble divalent metal salts would be potentially valuable sources of the metals if they could be solubilised or leached economically.

In our copending United Kingdom Patent Application 9819458.2 we have described novel water soluble complexes of divalent metals with tris (hydroxymethyl) phosphine (THP) and ammonia.

These complexes permit insoluble deposits to be solubilised and valuable metals to be recovered therefrom. We have devised a composition for use in solubilising water insoluble divalent metal deposits, which provides THP and ammonia. We have, however, discovered that THP reacts with ammonia and that the mixture is therefore unstable. We have discovered that the corresponding salts, tetrakis (hydroxymethyl) phosphonium salts and ammonium salts, do not react together under sufficiently acidic conditions.

The invention provides a composition comprising: (A) at least 0.01% by weight of a tetrakis (hydroxymethyl) phosphonium salt; (B) an ammonium salt in a ratio of A: B of from 0.01 to 100: 1 (C) sufficient of an acid which is substantially unreactive with tetrakis (hydroxymethyl) phosphonium ion or ammonium ion, to maintain the pH below 4:5; and (D) either sufficient of an aqueous solvent to dissolve the other components or a particulate or porous solid diluent which may consist at least in part of component (C), in an amount sufficient to absorb said components (A) and (B). All references herein to pH, as applied to solid compositions of the invention, are to be construed as referring to the pH of a 1% by weight solution of said composition in water at ambient temperature, or such higher temperature as may be required to obtain a 1% solution, or a hot saturated solution at 100°C or such lower temperature as may be required to obtain a stable solution where the saturation concentration of the composition or its acid component is less than 1% by weight, even at elevated temperature.

The water soluble tetrakis (hydroxymethyl) phosphonium salt (A) may be the sulphate (THPS), the chloride (THPC) or the phosphate. Alternatively the salt may be a salt of any other acid which does not react with the phosphonium ion, such as bromide, phosphite, formate, acetate, trichloracetate, borate or sulphite. However, preferably it is a salt of a strong acid which is not displaced at the pH of the composition. Preferably the concentration of A in the composition is greater than 1% by weight, usually greater than 5% by weight, more usually greater than 10% by weight, typically greater than 20% by weight, more preferably greater than 30% by weight, most preferably greater than 40% by weight, especially greater than 50% by weight, more especially greater than 60% by weight, e.g. 65 to 85% by weight, for instance 70 to 80% by weight.

The ammonium salt (B) may be any water soluble ammonium salt such as ammonium sulphate, ammonium chloride, or an ammonium salt of any of the other acids mentioned above in the context of the tetrakis (hydroxymethyl) phosphonium salt. Thus, the salt (B) may be ammonium
5 bromide, phosphite, formate, acetate, trichloracetate, borate or sulphite.

The weight ratio of component A to component B is preferably from 0.05 to 50:1, more preferably 0.1 to 30:1, most preferably 0.5 to 20:1, typically 0.6 to 10:1 especially 0.7 to 8:1, more especially 0.8 to 5:1,
10 e.g. 0.9 to 3:1.

The pH is preferably below 4.3, especially below 4, most preferably below 3.5, typically below 3, e.g. 0.1 to 2.5, for instance 0.5 to 2. The acid (C) may be sulphuric, hydrochloric, phosphoric or any of those
15 discussed above in connection with the salts, which is sufficiently strong to maintain the required pH. Thus the acid (C) may be hydrobromic acid, phosphorous acid, formic acid, acetic acid, trichloroacetic acid, boric acid or sulphurous acid. Conveniently A, B and D all comprise a common anion.

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The composition may additionally comprise other water treatment agents which are chemically compatible with A, B and C. For example: scale or corrosion inhibitors, such as 1-hydroxyethane-1,1-diphosphonic acid, amino methylenephosphonic acids, including amino tris
25 (methylenephosphonate), ethylenediamine tetrakis (methylenephosphonate), diethylenetriamine pentakis (methylenephosphonate), triethylene tetramine hexakis (methylenephosphonate) and higher homologues in the same series; ethanolamine bis (methylenephosphonate), phosphonocarboxylic acids, including phosphonosuccinic acid, and phosphonated telomers of
30 maleic, fumaric and/or acrylic acid, and copolymers of acrylic, maleic,

- vinyl phosphonic, vinyl sulphonic and/or vinyl diphosphonic acids; oxygen scavengers such as hydroxylamine; sequestrants such as sodium tripolyphosphate or potassium pyrophosphate; surfactants, including anionic, non-ionic, cationic and/or amphoteric surfactants; biopenetrants
- 5 such as quaternary ammonium polymers and copolymers, water soluble glycolethers and sulphonated aryl formaldehyde copolymers; antifoam such as silicone antifoams and acetylenic glycols; dispersants; flocculants; and/or biocides.
- 10 The composition may be an aqueous solution. According to a particular embodiment the composition may be obtained in solid form by coating the solution upon, or absorbing it into, a particulate or porous solid substrate. In a preferred embodiment a solution of (A) and (B) is coated onto or absorbed into a particulate or porous solid acid which constitutes
- 15 components (C) and (D).

The substrate should be chemically inert to component A and preferably acidic in character. Particularly preferred are organic fatty acids, dicarboxylic acids or hydroxy carboxylic acids such as maleic acid,

20 pimelic acid, suberic acid, azelaic acid, stearic acid, oleic acid, linoleic acid, palmitic acid, succinic acid, glutaric acid, or preferably, adipic acid. We generally prefer substrates with a melting point greater than 60°C, especially greater than 70°C.

- 25 The present invention also provides a method of making the composition hereinabove described. The solid composition may be obtained by spraying the solution, or separate solutions of A and B, onto the substrate, or by mixing the solution or solutions with the substrate and extruding, drying and pulverising the product. It is possible, though
- 30 usually less convenient, to prepare separate solids comprising A and B

respectively and mix them. The power may be compacted into granules or tablets, or may be enclosed in water soluble bags or sachets formed from a water-soluble, film-forming polymer, such as polyvinyl alcohol.

- 5 The present invention further provides the use of the composition to reduce the deposit of water-insoluble divalent metal salts in a water system.

The composition may be added directly to alkaline, neutral or weakly
10 acidic water systems (e.g. at pH down to 5) to dissolve or leach divalent metal, usually in a sufficient dosage to provide 0.1 to 1,000ppm THP in the system, more preferably 0.5 to 500ppm, e.g. 1 to 400ppm, especially 5 to 300ppm, more especially 10 to 200ppm, most especially 20 to 100ppm. It may be convenient, at least partially, to neutralise the acid
15 composition prior to addition to neutral or acidic water systems.

The invention is illustrated by the following examples.

Example 1

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An aqueous solution of 50% by weight THPS and 25% by weight ammonium sulphate was adjusted to pH1 with sulphuric acid. The composition was stable on storing.

- 25 The solution was dosed to an alkaline formation water in an oil well obstructed with ferrous sulphide deposits at a rate equivalent to 100ppm THPS. The ferrous sulphide dissolved as a bright red complex.

Example 2

5 A solution of 50% by weight THPS and 25% by weight ammonium sulphate was sprayed as a fine mist onto an air fluidised bed of powdered adipic acid at 40°C. The product was a free flowing powder containing 11% by weight THPS, 6 % by weight ammonium sulphate and 3% moisture. The product was stable on storage.

CLAIMS

1. A composition comprising:
 - 5 (A) at least 0.01% by weight of a **tetrakis(hydroxymethyl)phosphonium salt**;
 - (B) an ammonium salt in an amount such that the ratio of (A) to (B) is from 0.01:1 to 100:1;
 - 10 (C) a sufficient amount of an acid which is substantially unreactive with **tetrakis(hydroxymethyl)phosphonium ions** and with ammonium ions to maintain the pH of the composition below 4.5;
 - 15 (D) **either**: sufficient of an aqueous solvent to dissolve said components (A), (B) and (C)
 - or: a particulate or porous solid diluent, in an amount sufficient to absorb said components (A) and (B).
 - 20
2. A composition according to Claim 1, wherein said solid diluent consists, at least in part of said component (C).
3. A composition according to Claim 1 or 2, wherein said component
25 (A) consists essentially of **tetrakis(hydroxymethyl)phosphonium sulphate**, chloride or phosphate.
4. A composition according to Claim 1 or 2, wherein said component
30 (A) consists essentially of **tetrakis(hydroxymethyl)phosphonium bromide**, phosphite, formate, acetate, tri-chloroacetate, borate or sulphite.

5. A composition according to any one of the preceding claims, wherein the concentration of said component (A) ranges from greater than 1% by weight to greater than 60% by weight.
- 5 6. A composition according to Claim 5, wherein the concentration of said component (A) is in the range 65% to 85% by weight, for example 70% to 80% by weight.
7. A composition according to any one of the preceding claims,
10 wherein said component (B) consists essentially of ammonium sulphate or ammonium chloride.
8. A composition according to any one of Claims 1 to 6, wherein said component (B) consists essentially of ammonium bromide, phosphite,
15 formate, acetate, tri-chloroacetate, borate or sulphite.
9. A composition according to any one of the preceding claims, wherein the weight ratio of said component (A) to said component (B) is in the range 0.05:1 to 50:1, preferably 0.1:1 to 30:1, more preferably
20 0.5:1 to 20:1.
10. A composition according to Claim 9, wherein said ratio is in the range 0.6:1 to 10:1, preferably 0.7:1 to 8:1, more preferably 0.8:1 to 5:1, for example 0.9:1 to 3:1.
- 25 11. A composition according to any one of the preceding claims, wherein said component (C) consists essentially of sulphuric acid, hydrochloric or phosphoric acid.

12. A composition according to any one of Claims 1 to 10, wherein said component (C) consists essentially of hydrobromic acid, phosphorous acid, formic acid, acetic acid, tri-chloroacetic acid, boric acid or sulphurous acid.

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13. A composition according to any one of the preceding claims, wherein the pH of the composition is below 4.3, preferably below 4, for example below 3.5 and most preferably below 3.

10 14. A composition according to Claim 13, wherein the pH is in the range 0.1 to 2.5, for example 0.5 to 2.

15 15. A composition according to any one of Claims 1 to 14, wherein said component (D) comprises an aqueous solvent capable of dissolving said components (A), (B) and (C).

16. A composition according to any one of Claims 1 to 14, wherein said component (D) comprises a particulate or porous substrate which constitutes said components (C) and (D) of said composition.

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17. A composition according to Claim 16, wherein said substrate is chemically inert to said component (A).

18. A composition according to Claim 16 or 17, wherein said substrate
25 is acidic in character.

19. A composition according to Claim 16, 17 or 18, wherein said substrate consists essentially of one or more organic mono-carboxylic, di-carboxylic or hydroxy-carboxylic acids.

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20. A composition according to Claim 19, wherein said acid is selected from the group consisting of maleic acid, pimelic acid, suberic acid, azelaic acid, stearic acid, oleic acid, linoleic acid, palmitic acid, succinic acid, glutaric acid and adipic acid.

5

21. A composition according to any one of Claims 17 to 20, wherein said substrate has a melting point greater than 60°C, for example greater than 70°C.

10 22. A composition according to any one of the preceding claims, wherein said composition additionally contains one or more of the following water-treatment agents:

- (i) scale inhibitors
- 15 (ii) corrosion inhibitors
- (iii) oxygen scavengers
- (iv) sequestrants
- (v) surfactants
- (vi) bio-penetrants
- 20 (vii) antifoams
- (viii) dispersants
- (ix) flocculants
- (x) biocides

25 23. A method of making a composition according to any one of Claims 16 to 22, wherein said method comprises spraying a solution (or separate solutions) of said components (A) and (B) on to the substrate.

24. A method of making a composition according to any one of
30 Claims 16 to 22, wherein said method comprises mixing solutions of said

components (A) and (B) with the substrate and extruding, drying and pulverising the product.

25. The use of a composition according to any one of Claims 1 to 22 to
5 reduce the deposits of water-insoluble divalent metal salts in a water system.

26. Use according to Claim 25, wherein the composition is dosed into
the water system to provide a concentration of THP ion in the range 0.1
10 to 1000 parts per million (ppm).

27. Use according to Claim 26, wherein said concentration is in the
range 0.5 to 500ppm, preferably 1 to 400 ppm, for example 5 to 300 ppm.

15 28. Use according to Claim 26 or 27, wherein said concentration is in
the range 10 to 200 ppm, for example 20 to 100ppm.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F5/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Further documents are listed in the continuation of box C.



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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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